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EXAFS Analysis of Nanocatalysts

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Introduction: Catalysis of small gold particles has been the object of considerable attention in the past few years. Recent reports [1-3] show that the catalytic activity of Au particles is highly sensitive to the structure of Au. The objective of our work is to investigate different synthesis techniques and support materials (MCM-41, and TiO_2) to prepare monodispersed Au by analyzing the material at several stages of preparation using the X-ray Absorption Fine Structure (EXAFS) technique.

Methods and Materials: A coassembly synthesis was used to directly dope gold nanoparticles on MCM-41 materials, while the wet impregnation method was employed to load gold on TiO_2 supports. The bifunctional amine silane ligands were used in the coassembly synthesis to immobilize gold precursors. Au L_{III}-edge EXAFS spectra were recorded at 90 K in transmission and fluorescence mode using a channel cut Si (111) monochromator. The program XDAP – version 3.2 was used to analyze and fit the data as described in the literature [4].

Results: Figure 1 shows the absolute parts of the Fourier-transformed $\chi(k)\cdot k^3$ Au L_{III}-edge EXAFS functions in the range of 3.0 $Å^{-1} < k < 17.4$ $Å^{-1}$ of the Au catalysts supported on MCM-41(a), and TiO_2(b) at different stages of preparation. For the Au nanocatalyts supported in MCM-41, the first peak at 2.04 Å (phase-corrected) is attributed to the Au-N coordination. This peak decreases after a series of reduction and calcination steps and finally disappears. In the case of Au-TiO_2, the first peak is shifted to 1.99 Å (phase-corrected) and is attributed to interactions of Au-O since the amine functional ligand is not present. In both cases, the second peak is located at the same distance as the one found for Au foil and is attributed to Au atoms in the first coordination sphere at 2.86 Å (phase-corrected). The results presented by the MCM-41 catalysts show that Au atoms aggregate with each other forming metallic particles since the increase of the magnitude of the second peak (Fig.1a) corresponds, in this case, to higher coordination numbers. The Au-Au coordination number is related to particle aggregation and subsequently particle size. Fitting analysis of the MCM-41 series revealed that the Au-Au coordination number increased from 4.5 (after reduction at 100°C) to 11 (after calcination at 540°C), which is very close to the value of 12 expected for bulk Au metal. The Au-TiO_2 catalysts showed a very distinct trend with formation of oxidic gold species (presence of Au-O shell) and weak Au-Au interactions (Fig.1b). A very small Au-Au coordination number (1.3) was obtained for the Au-TiO_2 calcined at 200°C, which indicates the presence of few Au atoms in the metallic phase and/or formation of small metal particles.

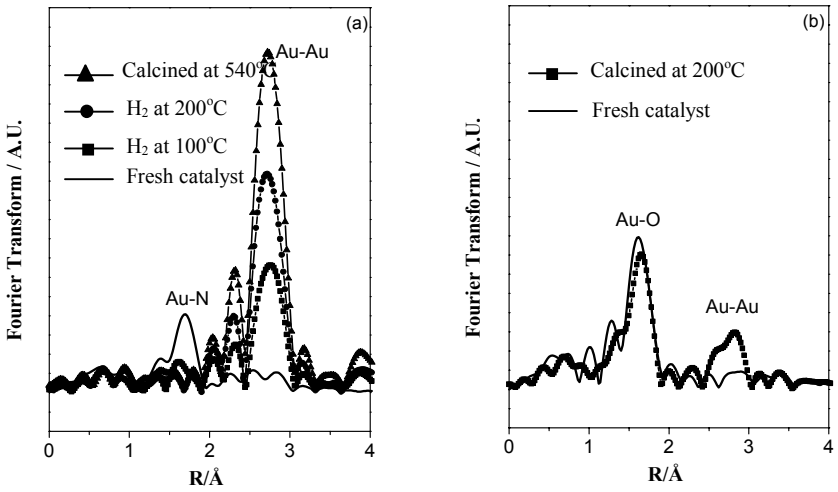

Figure 1: Au L_{III}-edge k^3 weighted Fourier Transform of the EXAFS of Au-MCM41(a) and Au-TiO_2 catalysts (b)

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